

## REMARKS

### Comments on Amendments

Claim 1 has been amended to specify the removal of the carbon dioxide from the gas stream is accomplished in a single absorption zone having from 5 to 80 contacting trays, and that the ratio of aqueous washing solution to gas is from 2 to 6 on a weight/weight (w/w) basis . Support for these amendments is found on page 7 of the specification, lines 14-21.

Claims 1 and 15 have been amended to recite the preferred concentrations of water, sulfolane and amine in the aqueous washing solution. Support for these amendments is found on page 5 of the specification, lines 1-7.

Claim 15 has been further amended to specify that Applicants' unique aqueous washing solution, after exposure to carbon dioxide, remains substantially free of insoluble carbamates. Support for this amendment is found on page 3 of the specification, lines 7-18, wherein it is disclosed that contrary to the teachings of the prior art, surprisingly insoluble carbamates are not formed when the unique amine/water/tetramethylenesulfone (sulfolane) mixtures of the present invention are used to absorb carbon dioxide.

Claim 16 has been canceled in view of the incorporation of the limitations of this claim into claim 15.

Claim 24 has been amended to recite one of the advantages of the present process in being able to produce carbon dioxide at intermediate pressures between 3 and 15 bara, as discussed on page 4 of the specification, lines 11-16.

Claim 27 has been amended to recite a preferred intermediate pressure range at which carbon dioxide can be produced using the present process. The recited range of between 5 and 10 bara is disclosed on page 4 of the specification, line 16.

### *Claim Rejections – 35 USC § 112*

#### **The Rejection of Claims 1-4, 9, 12-16, 20 and 23-27 under 35 U.S.C. § 112, First Paragraph, in Failing to Comply with the Written Description Requirement is Respectfully Traversed**

Applicant believes the term “a single absorption stage” is supported by the disclosure in the Example on pages 9 and 10 of the present specification. In the Example the unique

advantages of the present process in enhanced carbon dioxide removal were demonstrated in a commercially available standard absorber (page 9, lines 1-2). Such standard absorbers typically have a single absorption stage.

However, in order to remove this as an issue and to expedite allowance of the claims, Applicant has amended claim 1 to replace the terminology objected to by the Examiner with the limitation that the carbon dioxide-containing gas be washed with the aqueous washing liquid in an absorption zone having from 5-80 contacting trays, which terminology is clearly supported by the disclosure on page 7 of the present specification, lines 14-17.

The objection to claim 15 is believed obviated by the amendment specifying that it is Applicant's unique washing solution having the composition specified on page 5, lines 1-5, that is contacted with the carbon dioxide-containing gas resulting in a carbon dioxide loaded aqueous washing solution without the formation insoluble carbamates, contrary to the teachings in the art. Thus, amended claim 15 specifies the composition of the aqueous washing solution before loading with carbon dioxide, which is clearly supported by the disclosure on page 5 of the specification, lines 1-7. The fact that carbon dioxide is absorbed (i.e., removed) by the claimed composition without substantial formation of insoluble carbamates is supported by the disclosures page 3 of the specification, lines 7-18, wherein Applicants surprising finding is discussed.

For the above reasons, it is respectfully submitted that the amended claims fully comply with the requirements of 35 U.S.C. § 112. Accordingly, it is requested that the rejection of the claims under 35 U.S.C. § 112 be withdrawn.

### ***Claim Rejections – 35 USC § 103***

**The Rejection of Claims 1-4, 9, 12-16, 20 and 23-27 under U.S.C. 103(a) as Being Unpatentable Over Wagner et al (US 7,276,153) (“Wagner ‘153”) in view of Wagner et al (US 4,997,630) (“Wagner ‘630”), Evidenced by Grossmann et al (US 6,436,174) (“Grossmann”), is Respectfully Traversed**

### **The Presently Claimed Invention**

The presently claimed invention relates to a process for removing carbon dioxide from streams containing high concentrations of carbon dioxide by use of a unique aqueous washing

liquid in a specific ratio of washing liquid to the carbon dioxide-containing gas. The composition of the unique aqueous washing solution employed in the inventive process is recited in independent claims 1, and 15. The unique washing liquid contains between 20 and 45 parts by weight water, between 20 and 35 parts by weight of sulfolane, between 40 and 55 parts by weight of an amine selected from the group consisting of MEA, DEA, TEA, DIPA and MDEA, and from 0.7 mol/l to 0.9 mol/l piperazine. This aqueous washing fluid is employed at a ratio of between 2 and 6 (weight/weight) relative to the carbon dioxide-containing gas. This aqueous washing liquid to gas ratio is recited as a limitation in amended claim 1.

It has been found that contrary to teachings in the prior art, a mixture of water and a specific physical solvent, i.e., sulfolane, can be used at a relatively high concentrations in conjunction with piperazine and certain other amines without the formation of undesirable insoluble carbamates. See page 3 of the specification, lines 5-19, wherein the teachings of US 4,336,233 are discussed. Applicant is relying on teachings of US 4,336,233 as evidence of the unobviousness of process claimed in present claim 1 and the unique aqueous washing solution claimed in claim 15.

The Examiner's attention is drawn to column 3, lines 29-35 of US 4,336,233 wherein it is stated "that amongst industrially used physical solvents, e.g., methanol, mixtures of cyclotetramethylenesulfone, DIPA and water (Sulfinol ® ), NMP and dimethyl ethers of polyethylene glycols (Selexol ® ), only very dilute aqueous solutions can be used together with piperazine, because of the formation of piperazine carbamate." (emphasis added). Applicant has surprisingly found that such limitations do not occur when mixtures of water/sulfolane in certain proportions are employed with piperazine and an amine such as MDEA.

Applicant acknowledges that sulfolane and the amines recited in present claims 1 and 15 are generally known in the art and have been used in the art for the removal of acidic gases such as carbon dioxide and hydrogen sulfide from gas streams containing such acidic components. However, to Applicant's knowledge sulfolane and amines have never actually been used together with piperazine for the treatment of gases containing significant amounts of carbon dioxide, perhaps out of concern for possible formation of insoluble piperazine carbamate as reported in US 4,336 233.

The benefits of using Applicants' unique washing solution over the absorbent solutions taught in the prior art are discussed on page 4 of the present specification, lines 3-13, and demonstrated in the Examples on pages 9-10 of the specification. The benefits include faster

carbon dioxide absorption rates resulting in higher CO<sub>2</sub> loadings, lower solvent/gas ratios allowing smaller plant size and lower regeneration heat requirement.

Another important benefit of the present process is that the addition of sulfolane to the aqueous amine absorbent solution allows for the production of carbon dioxide at intermediate pressures, e.g. between 3 and 15 bara, preferably between 5 and 10 bara (specification, page 4, lines 13-16). This important aspect of the present process, which is not disclosed in any of the cited references, is now claimed in amended claims 24 and 27.

The specific combination of limitations that Applicant is relying for patentability over the prior art include removing high levels of carbon dioxide from a gas stream using an aqueous washing solution containing between 20 and 45 parts by weight water, between 20 and 35 parts by weight sulfolane and between 40 and 55 parts by weight of an amine selected from the group of amines consisting of MEA, DEA, TEA, DIPA and MDEA, and from 0.7 mol/l to 0.9 mol/l; employing an aqueous washing liquid to gas ratio of between 2 and 6, to remove carbon dioxide to low levels, without the formation of undesirable insoluble carbamates. Applicant is also relying on the limitations in claims 24 and 27 regarding the production of carbon dioxide at intermediate pressures of between 3 and 15 bara, and between 5 and 10 bara, as an additional basis of patentability.

It is respectfully submitted that the aforementioned underlined limitations would not be obvious from Wagner '153, alone or in combination with Wagner '630 and/or Grossman, for the reasons discussed below.

### **Wagner '153**

Wagner '153 discloses a process for deacidifying a fluid hydrocarbon stream containing carbon dioxide and/or other acidic gases in which the fluid stream is brought into contact with an absorption liquid in an absorption or extraction zone so the carbon dioxide can be absorbed by the absorption liquid. The absorption liquid is subsequently regenerated in two low pressure regeneration steps (col. 3, lines 40-65).

As stated on page 4 of the subject Office action, Wagner '153 does disclose that varied absorption liquids can be employed, with aqueous amine solutions containing at least one amine being preferred. Very particularly preferred is an absorption liquid comprising methyldiethanolamine (MDEA) used together with piperazine (col. 5, lines 37-38).

While Wagner et al, teaches two of the components employed in Applicant's aqueous washing liquid (MDEA and piperazine), Wagner '153 does not teach the use of a physical solvent. This is particularly interesting, since the inventors on Wagner '153 certainly knew about physical solvents such as sulfolane and N-methylpyrrolidone (NMP), since these physical solvents are specifically discussed in the background section of Wagner '153 (col. 1, lines 53-60). The fact that inventors on Wagner '153 knew of physical solvents, but did not employ them in their absorption liquid, if anything, supports the unobviousness of the present compositions.

In addition to not teaching the use of an aqueous absorption liquid containing sulfolane, the '153 patent does not teach an aqueous washing liquid to gas ratio of from between 2 and 6, which is recited as a limitation in amended claim 1.

On page 5 of the subject Office action, the Examiner points to the disclosure in column 2, lines 35-42 of Wagner'153 as suggesting the aqueous washing liquid to gas ratio of between 2 and 6. In the portion of Wagner '153 cited on page 5 of the subject Office action, it is taught that:

“Because of the slow reaction of carbon dioxide, the scrubbing process must be carried out using a high liquid/gas ratio at a corresponding high solvent recirculation rate. Therefore, attempts have been made to increase the absorption rate of carbon dioxide in aqueous solutions of tertiary alkanolamines by adding further compounds which are termed activators or promoters.”

Wagner '153 goes on to disclose that one of currently most effective absorption liquids for CO<sub>2</sub> and H<sub>2</sub>S is MDEA and piperazine as an absorption activator (col. 2, 44-48). Therefore, not only does Wagner '153 fail to teach the specific liquid to gas ratio of between 2 and 6 specified in claim 1, but Wagner'153 suggests that the use of high liquid/gas ratios can be avoided by using an absorption activator such as piperazine.

Applicant believes the criticality of the recited liquid to gas ratio of between 2 and 6 has been demonstrated in the Example on pages 9 and 10 of the present application. Please note that excellent carbon dioxide removal results were obtained in the Example using a liquid/gas ratios of 4.4 and 3.1, both of which ratios are within the between 2 and 6 liquid/gas ratio specified in amended claim 1. Thus Applicant has established a criticality for the recited ratio.

Applicant respectfully submits that in the absence of a teaching in Wagner '153 of the specific concentration ranges for water, sulfolane and amine recited in amended claim 1, or that a physical solvent such as sulfolane is advantageous, and in the absence of a teaching of an

aqueous washing liquid to gas ratio of between 2 and 6, or that sulfolane in relatively high concentration does not cause the formation of insoluble carbamates, the presently claimed subject matter would not be obvious from Wagner '153. Applicant will now explain why neither Wagner '630 nor Gossmann overcome the deficiencies in Wagner '153.

### **Wagner '630**

Wagner '630 discloses a process for removing CO<sub>2</sub> and/or H<sub>2</sub>S from gases using an aqueous alkanolamine-containing absorption liquid, wherein the gas is treated in a first absorption stage at 40° to 100° C, with an aqueous absorption liquid containing from 20 to 70 % by weight of methyldiethanolamine (MDEA). The gas obtained at the top of the first absorption stage is fed to a second absorption stage where it is treated at 30 to 90°C with an aqueous absorption liquid containing from 20 to 70 % MDEA to effect further removal of CO<sub>2</sub> and H<sub>2</sub>S. The treated gas is taken off the top of the second absorption stage, while the aqueous absorption solution from the bottom of the second absorption stage preladen with CO<sub>2</sub> and/or H<sub>2</sub>S is fed to the top of the first absorption stage. The aqueous absorption liquid obtained from the bottom of the first absorption stage laden with CO<sub>2</sub> and/or H<sub>2</sub>S is let down in two or more flash stages in order to regenerate it (col. 1, lines 21-44).

In the sole example in the Wagner '630 reference, a CO<sub>2</sub>-containing synthesis gas was washed with a 50 % strength by weight aqueous methylenediethanolamine (MDEA) solution as the absorption liquid (col. 6, lines 56-59). This is the only specific absorption liquid disclosed in the Wagner et al reference. While the amine component (50 % strength by weight methylenediethanolamine) meets the between 45 and 55 parts by weight amine limitation in amended claims 1 and 15, the absorption liquid used in the example does not contain sulfolane, does not contain piperazine and contains 50 % by weight water, which is outside the 20 to 45 parts by weight water limitation in the present claims.

Applicant acknowledges there are other disclosures in the Wagner '630 reference on which the Examiner relies for his obviousness rejection. However, as discussed below, these other disclosures do not teach or reasonably suggest the unique combination of features recited in the present claims.

For example, the feature that the present claims the absorption solution contain between 20 and 35 parts by weight of sulfolane. Wagner '630 in its most relevant aspects teaches that the

aqueous absorption liquid containing from 20 to 70 % by weight of methyldiethanolamine, “can additionally” contain a physical solvent, and then goes on to list a number of physical solvents, including N-methylpyrrolidone, tetramethylene sulfone, methanol, oligoethylene glycol dialkyl ethers such as oligoethylene glycol methyl isopropyl ether (SEPASOLV MPE) or oligoethylene glycol dimethyl ether (SELEXOL) (Wagner ‘630, col. 2, lines 44-51) . Wagner ‘630 gives no specific examples where physical solvents are actually added to the absorption solution, and treats all of the listed physical solvents (if added at all) as being interchangeable. Furthermore, there is absolutely no recognition of the surprising discovery made by Applicant that relatively high concentrations of sulfolane in the absorption solution does not cause insoluble carbamate formation when exposed to carbon dioxide, contrary to the teachings of the prior art. The fact that the carbon dioxide loaded aqueous washing solution in Applicant’s process is substantially free of insoluble carbamates is recited as a limitation in both independent claims 1 and 15.

In marked contrast to the optional “can additionally contain” language in Wagner ‘630, Applicant’s aqueous washing solution is required to have a physical solvent and that physical solvent is required to be sulfolane. Also, Applicant employs sulfolane at concentrations that at least one prior art patent (US 4,336,233) suggests may result in insoluble carbamate formation, which Appellant surprisingly found was not the case, as discussed above.

Therefore, in its most relevant aspects Wagner ‘630 teaches the optional addition of a variety of different physical solvents, while never actually using a physical solvent in any specific examples. Moreover, Wagner ‘630 does not overcome the other deficiencies of Wagner ‘153 in not teaching aqueous washing liquid to gas ratios of between 2 and 6, and not suggesting Applicant’s discovery that sulfolane can be used in relatively high concentrations without insoluble carbamate formation. Furthermore, Wagner ‘630 does not teach the production of carbon dioxide at the intermediate pressures recited in amended claims 24 and 27.

## **Grossmann**

Grossmann discloses a process for removing acidic constituents from gases in an absorption step in which an untreated gas rich in acidic gas constituents is brought into contact an absorption medium comprising a mixture comprising: a) 0.1 to 50 wt% of one or more mono-cyclic or bicyclic nitrogen heterocycles, b) from 1 to 60 wt% of a monohydric and/or polyhydric alcohol, c) from 0 to 60 wt% of an aliphatic alkanolamine, d) from 0 to 98 wt% water, and e)

from 0 to 35 wt%  $K_2CO_3$  (col. 1, line 57 to col. 2, line 11). The disclosed absorption medium bears little resemblance to the aqueous washing liquid employed in Applicant's claimed process, or the processes described in Wagner '153 or Wagner '630. Apparently Grossman is being cited as evidence that adding physical solvent to increase the absorption rate as well as the absorption capacity is known in the art. This may be true. However, Applicant is not broadly claiming physical solvents in combination with chemical solvents. The present claims are directed to a very specific aqueous washing liquid containing specific amounts of a specific physical solvent (sulfolane), specific amounts of one of five specific amines, together with specific amounts of piperazine. Moreover, sulfolane is used in a concentration range that the prior art suggests may cause insoluble carbamates to form if the washing liquid is used to treat gases containing high levels of carbon dioxide. Applicant has surprisingly found this not the case.

It is the combination of features including a narrowly defined aqueous washing liquid, a washing liquid to gas ratio of between 2 and 6, and the absence of insoluble carbamate formation that is not taught or reasonably suggested by Wagner '153 or Wagner '630. Grossmann does nothing to overcome these deficiencies in the two Wagner references. Nor does Grossmann teach the production of carbon dioxide at intermediate pressures within the ranges recited in amended claims 24 and 27.

## **Conclusion**

For all of the above reasons and in view of the amendments and the showing in the Example, remaining claims 1-4, 9, 12-15, 20 and 23-27 as amended, are believed to be patentable over cited references. Accordingly, reconsideration and favorable action on the application is respectfully requested.

Respectfully submitted,

THEODORUS J. BROK, RUDOLF J. M. GROENEN,  
JEANINE M. KLINKENBIJL and MARIETTE C. KNAAP

By /Charles W. Stewart/  
Their Attorney, Charles W. Stewart and  
Leonard P. Miller  
Registration Nos. 34,023 and 26,004  
(713) 241-0360

P. O. Box 2463  
Houston, Texas 77252-2463